

## Electrogravimetric and Chronoamperometric Monitoring of Individual Events of Growth and Detachment of Electrolytic Chlorine Gas Bubbles

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A simultaneous electrogravimetric and chronoamperometric approach is reported which enables individual events of growth and detachment of electrolytic gas bubbles to be monitored continuously.

The growth and detachment of gas bubbles from a solid/liquid interface are widely encountered in physicochemical processes, ranging from beverage cooling to distillation (under the predominant condition of heterogeneous nucleation) and industrial electrolysis. Important examples from the last class include the cathodic evolution of hydrogen and the anodic evolution of oxygen and chlorine. The hydrogen and oxygen processes became more important recently in view of the prospective large-scale electrolysis of water<sup>1</sup> to produce pollution-free fuels. The chlorine process constitutes the basis of the chlor-alkali industry,<sup>2</sup> the world's largest electrochemical industry.

The classic method widely used in previous studies of electrolytic gas bubbles<sup>3</sup> involves the measurement and interpretation of the overall current,<sup>4</sup> which yield information about the collective behaviour of numerous bubbles. The photographic approach<sup>3,5</sup> is capable of documenting individual bubbles directly, but the pictures may not be correlated in a straightforward way with the simultaneous electrochemical signals. The recent method using an electrochemical quartz crystal microbalance (EQCM),<sup>6-8</sup> on the other hand, has the advantage of affording an additional parameter, the resonant frequency,  $f$ . Since  $\Delta f$  values corresponding to sub-nanogram mass change,  $\Delta m$ , at the electrode surface, can be detected easily, the EQCM is sensitive enough to 'weigh' single bubbles continuously, while the electrochemistry is being studied simultaneously. In this communication, the EQCM technique is combined with microscopic inspection and a special procedure of current recording to examine the process of chlorine evolution.

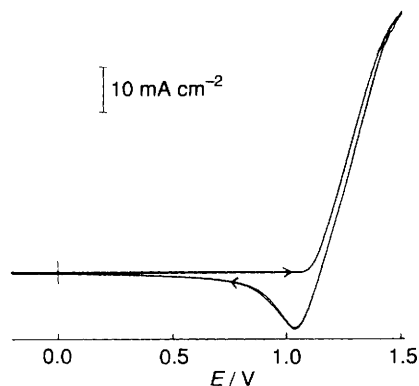
Chlorine gas bubbles were generated in aqueous chloride solutions on a Pt disc anode (area 0.2 cm<sup>2</sup>), which also served as the contact of the EQCM whose construction has been described previously.<sup>7</sup> A saturated calomel electrode (SCE) was used as the reference electrode. A glass pocket was attached to the outside of the electrolytic cell and was filled with the same electrolyte as used inside for electrolysis. Through this window, which minimizes image distortion

caused by the cell wall, inspection with a microscope (tenfold magnification) was carried out to monitor the location, number and timing of bubbles which are growing or detaching, and the correlation of the events with the simultaneous changes in current and mass.

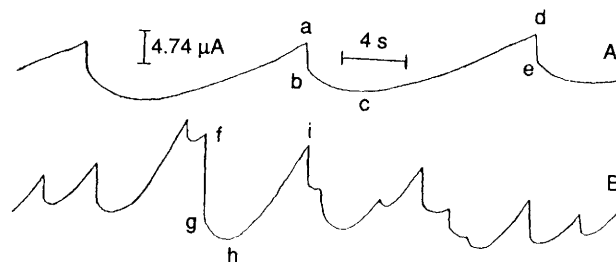
The broad  $i$ - $E$  features of the chlorine evolution can be seen from the cyclic voltammograms shown in Fig. 1. Chloride oxidation starts from ca. 1.07 V and is accelerated significantly at more positive potentials. Formation of bubbles begins at potentials around 1.2 V (it is lower under potentiostatic conditions) and intensifies as the potential is swept anodically. The magnitude of the cathodic peak at ca. 1.04 V indicates a significant solubility of molecular chloride in the solution, which leads to bubble efficiency lower than the faradaic efficiency of the  $\text{Cl}^- \rightarrow \text{Cl}_2$  process, which is estimated to be >95% under the conditions given.

For potentiostatic evolution of chlorine, the electrode potential was finely tuned and selected in such a way that only a limited number (ideally one) of reaction sites on the electrode surface are active for bubble nucleation and growth at a time, so that the bubble events are separated in time and space and individual bubbles can be investigated in detail with minimal interference from other bubbles. Such a situation was directly confirmed by inspection with the microscope. The bulk of the current output, resulting mainly from chloride discharge, was offset by a selected dc potential from an external voltage source, and the remaining part reflecting the bubble's activities was 20-fold amplified before being recorded. Fig. 2 shows the current-time transients during chlorine bubble evolution recorded in this way. Simultaneous inspection with the microscope confirms that the current changes are caused by individual events of growth and detachment of bubbles: the current decreases (e.g. sections cd and hi of Fig. 2) as the bubbles grow bigger, and increases steeply (sections ab, de, fg etc.) as expected when the bubbles detach. The detailed  $i$ - $t$  relationship is consistent quantitatively with the nucleation and growth theory.<sup>9</sup> Compared with the signal of resistance,<sup>10</sup> therefore, the current signal can be used for kinetic analysis of the process down to the level of a single bubble. Details of the analysis will be presented elsewhere.

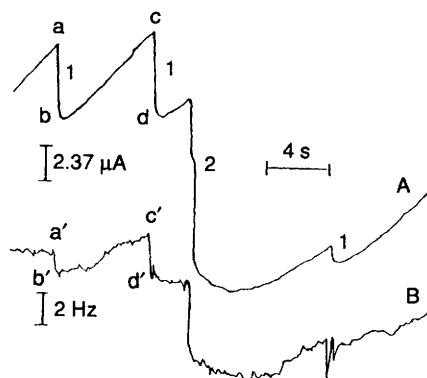
Fig. 3 shows a set of  $i$ - $t$  and the simultaneous  $\Delta f$ - $t$  curves during chlorine evolution at a constant potential. Here again, the changes in current and mass are related to individual



**Fig. 1** Cyclic voltammograms for the chlorine evolution process. The aqueous electrolyte contained 0.9 mol dm<sup>-3</sup> NaCl and 0.1 mol dm<sup>-3</sup> HCl. The sweep rate was 20 mV s<sup>-1</sup>. Two consecutive cycles are shown. The downward curvature near the anodic end of the scan is due to output saturation of the potentiostat and the apparent absence of hydrogen peaks near the cathodic end is due to the current scale used.



**Fig. 2** Current-time curves during the potentiostatic evolution of chlorine bubbles. The electrode potential was held constant at 1.180 (A) and 1.206 (B) V vs. SCE. The electrolyte was the same as in Fig. 1. Note that going down the page corresponds to an increase in anodic current. Section fg resulted from concurrent detachment of two chlorine bubbles, whereas all the other vertical sections were associated with the detachment of one bubble.



**Fig. 3** Current and EQCM frequency changes as a function of electrolytic time. A ( $i$  vs.  $t$ ) and B ( $\Delta f$  vs.  $t$ ) were recorded simultaneously. The electrode potential was held constant at 1.184 V vs. SCE. The electrolyte was the same as in Fig. 1. The numbers on A indicate the number of bubbles detached. Going down the page corresponds to an increase in anodic current (A) or electrode mass (B).

bubbles. As the bubbles grow continuously, a progressively larger portion of the heavier liquid electrolyte bathing the electrode surface is replaced by the lighter chlorine gas bubbles which block the space near the electrode surface for charge transfer and diffusion, resulting in a decrease in both the current (section bc) and the mass (section b'c'). When bubbles detach, the solution collapses into the vacancy left by the bubbles, and a sudden increase in mass is observed (e.g. section c'd'). Meanwhile, the effective electrode area is increased and the filling solution is less depleted with respect to the reactant ( $\text{Cl}^-$ ) and less saturated with respect to the product ( $\text{Cl}_2$ ) of the electrode reaction, a current increase is seen (section cd). The clear similarity between curves A and B of Fig. 3 indicates the consistency of mass changes sensed by the EQCM with the current changes. The magnitude of the frequency changes indicates the mass sensitivity of the EQCM technique. Typically, 2–10 ng of mass change per bubble is detected. This information, combined with the size and contact angle of the bubbles measured *in situ* through the microscope, and the simultaneous electrochemistry, can

provide more fundamental knowledge of the phenomena of electrolytic bubbles.

In conclusion, the EQCM technique is shown to be capable of continuously monitoring the individual events of growth and detachment of electrolytic chlorine gas bubbles, owing to its great mass sensitivity in conjunction with a careful control of electrode potential. The mass signal can be correlated quantitatively and simultaneously with the electrochemical parameters to provide a further insight into the electrolytic bubbling processes.

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### Footnote

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